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DETONATION PRODUCTS OF OXYGEN
DEFICIENT EXPLOSIVES (U)

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25 OCTOBER 1965

UNITED STATES NAVAL ORDNANCE LABORATORY, WHITE OAK, MARYLAND

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18 NOLTR-65-114
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(6) DETONATION PRODUCTS OF OXYGEN DEFICIENT EXPLOSIVES (U),

(10) C. B. Root and J. N. Ayres.

Mild detonating fuse containing oxygen deficient explosives such as DIPAM and RDX showed considerable formation of carbon monoxide when fired in the absence of atmospheric oxygen. As might be the case in space or high altitude applications, and depending on the total amount of explosive, the detonation products of MDF loaded with oxygen deficient explosives could contain sufficient carbon monoxide to be harmful to human beings. A method is given for estimating the toxicity from carbon monoxide and carbon dioxide when oxygen deficient explosives are detonated in confined structures.

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EXPLOSIONS RESEARCH DEPARTMENT
U.S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

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22

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25 October 1965

DETONATION PRODUCTS OF OXYGEN DEFICIENT EXPLOSIVES (U)

This work was performed as a result of interest in the products of detonation of a heat resistant explosive, DIPAM. This explosive has application on the Navy F-111 aircraft and possible application on NASA spacecraft. Investigations are being made to determine the usefulness of new heat resistant explosives in explosive components for future space programs like APOLLO. This report discusses possible hazards from DIPAM and RDX fired in oxygen deficient atmospheres.

The identification of commercial materials implies no criticism or endorsement by the U. S. Naval Ordnance Laboratory.

J. A. DARE
Captain, USN
Commander

(Signature)
C. J. ARONSON
By direction

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TABLE OF CONTENTS

	Page
INTRODUCTION	1
DETERMINATION OF GASEOUS DETONATION PRODUCTS	
Apparatus	2
DISCUSSION	2
Solid Detonation Products	5
Chamber Temperature Studies	8
CONCLUSIONS	13
RECOMMENDATIONS	15

TABLES		
Number	Title	Page
I	STUDY OF GAS ENVIRONMENT EFFECT ON DECOMPOSITION PRODUCTS, TEST CONDITIONS AND RESULTS	4
II	DIPAM-MDF SOLID PRODUCTS VS ATMOSPHERIC OXYGEN	7
III	TEMPERATURE STUDY RESULTS	11

FIGURES		
Number	Title	Page
1	APPARATUS FOR THE COLLECTION OF GASEOUS DETONATION PRODUCTS	3
2	TEMPERATURE PROFILES OF GAS ANALYSIS FIRINGS	9
3	TEMPERATURE STUDY APPARATUS	10
4	TEMPERATURE STUDY RESULTS	12
5	EFFECT OF ATMOSPHERIC OXYGEN ON CO ₂ /CO BALANCE	14

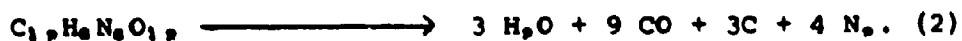
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INTRODUCTION

Most new and conventional military explosives are oxygen deficient, i.e., they do not contain enough oxygen in their molecular structure to convert the carbon and hydrogen present to water vapor and carbon dioxide. For example, RDX (hexahydro-1,3,5-trinitro-5-triazine) is slightly oxygen deficient. Assuming the formation of H_2O , C , CO , and CO_2 , in that order until all atoms of the reactant are utilized, it would give products as follows:



DIPAM (3,3'-Diamino-2,2',4,4',6,6'-Hexanitrobiphenyl) a new heat resistant explosive developed at NOL is representative of a highly oxygen deficient explosive. DIPAM would react as follows:



These simplified equations provide a very useful starting point for explaining the reaction products that actually occur. However, prevailing temperatures and pressures, the chemical species present, and the thermodynamic quantities of importance lead to complex mixtures of products. Afterburning (combination of partially oxidized detonation products with oxygen in the air) and other phenomena also complicate the picture. For example, the products of DIPAM loaded mild detonating fuse (MDF) have been noted to vary from black to light yellow in color depending upon detonation conditions.

DIPAM is being used in MDF and in flexible linear shaped charge (FLSC) for transmission of detonation from point to point and for cutting metals in missiles, aircraft, and spacecraft. In airplanes and spacecraft these operations are often carried out near the crew. According to the above equations a significant amount of carbon monoxide would be expected, particularly if there is little or no afterburning. Accordingly, we wished to determine what proportion of noxious or toxic gaseous products would be expected from the functioning of DIPAM-loaded MDF. We also wished to determine the effect of free volume and atmospheric oxygen on the make-up of the reaction products. Thus, the purpose of this work was to determine the nature of the products formed when oxygen deficient explosives are detonated in obturated mechanisms or structures using MDF or FLSC. Such information should be useful in deciding future applications of MDF and FLSC within capsules, space vehicles, and the like where the reaction products could impair human efficiency, or could even conceivably be lethal.

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DETERMINATION OF GASEOUS DETONATION PRODUCTS

Apparatus

The firing chamber used is shown in Figure 1. A piece of MDF was wound around the grooved aluminum cylinder and attached to a detonator as shown. The depth of the groove was greater than the outside diameter of the MDF to protect the unreacted MDF from fragments as the detonation moved around the cylinder. The detonator consisted of a bridgewire in contact with 30 mg of dextrinated lead azide, followed by a 40 mg base charge of DIPAM pressed into a charge holder. The amount of explosive in the detonator was small compared to the amount of explosive contained in the MDF. (This will be discussed later in the text.)

After firing, a sample of the gases present in the chamber was collected in an evacuated flask via valve A. A thermocouple placed as shown was used to monitor the temperature inside the chamber before and after detonation. All gas samples were taken when the chamber contents had cooled to 40°C. The chamber, while not sealed, was essentially air tight.

To establish in the chamber the nitrogen atmosphere used in some tests, the bottom cap was loosened and the chamber flushed with nitrogen at 10 psig (fed in through valve A) for 10 minutes. The pressure inside the chamber was allowed to come to equilibrium with atmospheric pressure and the system closed for firing. The gas samples were analyzed for CO₂, CO, N₂, H₂, O₂, H₂O, and hydrocarbon content by a mass spectrometer at the Bureau of Standards. A tabulation of experimental variables and gas analysis results for seven experimental firings are given in Table I.

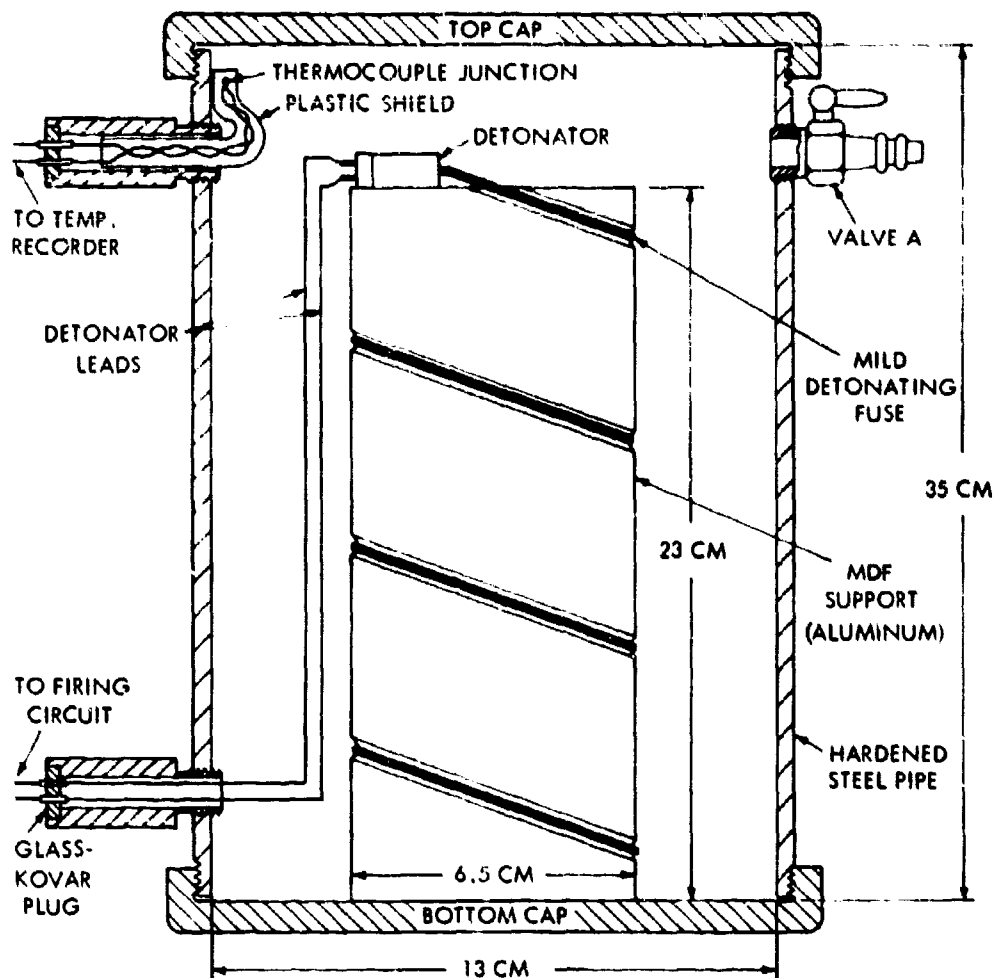
DISCUSSION

As shown in Table I, four DIPAM shots were fired and the gaseous products analyzed as described. The CO₂/CO ratio may be used as a rough index of the degree of afterburning which occurred. Since DIPAM is oxygen deficient we would not expect CO₂ to be formed unless oxygen were to be made available from some external source, note equation (2).

Sample A, the detonator alone fired in air, shows products so close to that of the room air composition that the contribution of the detonator to the overall product distribution was considered negligible. The same type of detonator was used in all shots.

The gaseous products from samples B and C show the difference in products when equal amounts of the same explosive

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VOLUME OF CHAMBER: 5.4 LITERS
TEST FIRED AT 25° C AND 750 mmHg

FIG. 1 APPARATUS FOR THE COLLECTION OF GASEOUS DETONATION PRODUCTS

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TABLE I
STUDY OF GAS ENVIRONMENT EFFECT ON DECOMPOSITION
PRODUCTS, TEST CONDITIONS AND RESULTS

	Test Identification						
	A	B	C	D	E	F	G
Fill Gas	Air*	N ₂	Air*	Air*	Air*	N ₂	Air*
Explosive	Detonator	DIPAM	DIPAM	DIPAM	DIPAM	RDX	RDX
MDF Core Load (grains/ft)	—	15	15	2.1	15	10	10
MDF Length (inches)	—	14	14	95	28	9.5	9.5
Quantity of grains	—	17.5	17.5	16.6	35.0	7.92	7.92
grams	0.070	1.134	1.134	1.077	2.268	0.513	0.513
Explosive moles	0.0002	0.0025	0.0025	0.0024	0.0050	0.0023	0.0023
Moles O ₂ in Chamber Atmosphere	0.045	0.0	0.045	0.045	0.045	0.0	0.045
Mole Ratio: O ₂ /Explosive	225	—	18	19	9	—	20
Mole Ratio CO ₂ /CO	2	0.5	65	35	1.2	0.8	65
Color of Solids	Grey	Black	Yellow-grey	Yellow-grey	Black	Grey	Grey
CO ₂	0.2	2.6	13.0	13.9	16.3	1.6	12.8
CO	0.1	4.9	0.2	0.4	13.1	1.9	0.2
H ₂ O	1.1	1.2	2.2	1.7	1.3	1.0	1.2
N ₂	76.8	88.6	77.2	77.2	64.3	92.3	81.3
O ₂	20.9	2.3	6.9	5.9	1.0	1.6	3.2
Ar	0.9	0.4	0.8	0.9	1.0	0.6	1.3
H ₂	—	—	—	—	2.7	1.0	—
C ₂ H ₂	—	—	—	—	0.3	—	—
*Gas Analysis of Environmental Air (mole %): H ₂ O=0.9; N ₂ =77.4; O ₂ =20.8; and Ar=0.9							

are fired in air and in nitrogen atmospheres. The free oxygen found in the products of the nitrogen atmosphere shot may have resulted from a sampling error, incomplete flushing with nitrogen prior to the firing, or even reentry of gas after firing and during the cooling to 40°C. Note that in sample B nearly all the available oxygen is utilized in the reaction, as is indicated by the reduction of the free oxygen from 20.8 to 2.3 mole per cent. This indicates considerable after-burning. The amount of carbon monoxide produced in the nitrogen atmosphere (Test B) is 4.7 mole per cent greater than in the air atmosphere (Test C). Thus the reaction product distribution seems to approach equation (2) when atmospheric oxygen is not available. A high carbon content in the products of the nitrogen shot is predicted by equation (2) and is verified by the black sooty residue found in the firing chamber. Sample A yielded a light grey residue.

As might be expected, the available atmospheric oxygen strongly affects the CO_2/CO ratio. As the available oxygen decreases the ratio decreases. Comparing samples C and D with sample E we find that the CO_2/CO ratio has changed from ~ 50 to ~ 1.2 as a result of doubling the total quantity of explosives detonated in the same free volume. Comparing sample E with sample B (no oxygen) the CO_2/CO ratio has further decreased to ~0.5.

Note that in sample E products not otherwise observed were found: acetylene and hydrogen. It is possible that these species were formed because this was a larger explosion with a more vigorous heat pulse that may have caused free radical combination not possible or detectable in the lower powered shots.

Samples C and D show that no significant difference in products results from different core load sizes of MDF. The sheath to explosive ratio in both shots was approximately the same as were the moles of explosive fired. Note the corresponding similarity of products and CO_2/CO ratio.

Two shots were fired using RDX loaded MDF. These show that RDX behaves in much the same manner as DIPAM when fired with and without atmospheric oxygen being present. The carbon monoxide content of the nitrogen atmosphere shot is not so pronounced as with DIPAM since RDX is less oxygen deficient. As predicted by equation (1) no significant free carbon was formed in the oxygen deficient atmosphere since RDX contains enough molecular oxygen to convert all of its carbon to carbon monoxide.

Solid Detonation Products

The solid products produced when DIPAM MDF is detonated

take the form of fine powder interspersed with small particles of free lead from the MDF sheath. Workers have observed smoke and solids varying in color from light yellow to sooty black. RDX, on the other hand, yields a grey powder under nearly all conditions of detonation.

A qualitative explanation of the above differences in products as a function of available oxygen in the atmosphere may be postulated. Sample B, DIPAM fired in N_2 , and sample E, DIPAM fired in limited O_2 , both exhibited black solid products containing free carbon. Samples C and D, DIPAM fired in excess air, exhibited lighter colored products with little or no free carbon. Thus, in an abundance of oxygen, most of the carbon not combined with molecular oxygen of the explosive does combine with the atmospheric oxygen to eliminate free carbon in the final products. The yellow hue noted in cases where excess oxygen is available is probably caused by the presence of yellow lead oxides formed by combination of the superheated lead sheath with atmospheric oxygen during detonation.

A series of shots was fired in an essentially closed tube in order to determine the oxygen/DIPAM ratio which causes the transition from light to dark products. The ratio of air to DIPAM was varied by firing different amounts of explosive in the same volume of air. The DIPAM-MDF was initiated external to the test chamber and then lead into it through a small hole. This eliminated the effects of an initiator. The experimental variables and results of this study are given in Table II.

The nature of the solid products changes between 1 and 2 moles of oxygen per mole of DIPAM. At greater concentrations of air very little carbon is produced, and at lower concentrations the residue is black indicating considerable unoxidized carbon. This seems to indicate that a corresponding increase in carbon monoxide present also starts to occur at this ratio of air to DIPAM since the presence of free carbon in the gas analysis shots correlated with higher carbon monoxide content in the gaseous products.

There is one possible inconsistency between these results and the ones shown in Table I:

Data from Table I		Data from Table II	
O_2/HE	Color	O_2/HE	Color
0	Black	0.67	Black
9	Black	1.0	Black
18	Yellow-Grey	2.0	Grey
19	Yellow-Grey	3.0	Yellow-Grey

TABLE II
DIPAM-MDF SOLID PRODUCTS VS ATMOSPHERIC OXYGEN

	Test Identification			
	R	J	K	L
MDF Core Load (grains/ft)	15	10	10	10
MDF Length (inches)	6	6	3	2
Quantity grains	7.5	5	2.5	1
of grams	0.486	0.324	0.162	0.108
DIPAM millimoles	1.057	0.714	0.357	0.239
Mole Ratio O ₂ /HE	0.67	1.0	2.0	3.0
Color of Solid Products	Black	Black	Grey	Yellow-Grey
Chamber Volume	85 milliliters			
Gas Content (STP conditions)	3.43 millimoles			
O ₂ Content (at 20.8 mole %)	0.713 millimoles			

Apparently the transition from black residues to yellow-grey occurs at a much higher O_2/HE mole ratio for the larger free volume experiment than for the smaller. However, the differences in the two experiments may well have caused such an apparent difference in results: the MDF in the Table I experiment is in direct contact with the surface on which the residue was collected while in the other it was at least a centimeter away. The direct contact could quench the reactions more quickly — thus requiring a greater amount of atmospheric oxygen to be present to sustain the reaction.

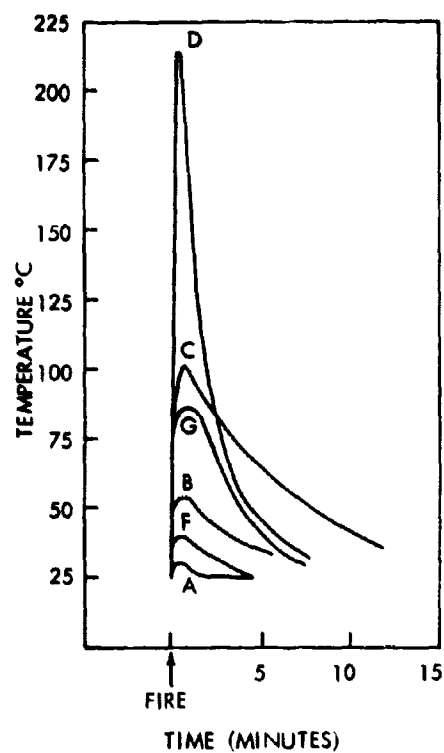
Chamber Temperature Studies

In order to be able to withdraw samples consistently at 40°C, the temperature inside the gas analysis test chamber was monitored during detonation. Figure 1 shows the thermocouple placement. The temperature-time profiles for the various shots are shown in Figure 2. As expected, the shots in the nitrogen atmosphere exhibit lower temperature-time profiles since there is no heating from afterburning. Considerable heat is apparently generated in the afterburning process. No data are available for sample E because the force of the detonation destroyed the thermocouple. The high chamber temperature recorded for the small diameter DIPAM MDF (sample D) prompted a series of temperature study shots. These were designed to determine whether higher temperatures were generally achieved from small diameter MDF.

Figure 3 shows the apparatus used to determine the temperature of the gases given off when various sizes of MDF were fired. Redundant thermocouples were used to measure the temperature of the detonation products forced through the vent holes in the end of the chamber. The 90° bend in the chamber prevented shrapnel damage to the thermocouples. The detonator was placed outside the chamber so it would not contribute to the measured effects. The area of the vent holes was large compared to the hole through which the MDF was inserted. Thus, most products were vented past the thermocouple upon detonation of the MDF. Temperature was recorded as millivolts displayed on a calibrated dual beam oscilloscope equipped with a polaroid camera.

The results of firing six-inch sections of 2.1, 10, and 15 grains/ft DIPAM MDF are tabulated in Table III. The temperature observed was found to be proportional to the amount of DIPAM and/or the core load. (Figure 4) Had there been a disproportionately high temperature when the 2.1 grain/ft MDF was fired (as was indicated by test D of Table I) then we would not have expected to see the linear relationship shown in Figure 4.

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SAMPLE	MFD LENGTH (INCHES)	CORE LOAD (GRAINS/FT)	EXPLOSIVE	TOTAL EXPLOSIVE (GRAINS)	GAS ENVIRONMENT
A	DETONATOR ONLY				AIR
B	14	15	DIPAM	17.5	N ₂
C	14	15	DIPAM	17.5	AIR
D	95	2.1	DIPAM	16.6	AIR
F	9.5	10	RDX	7.92	N ₂
G	9.5	10	RDX	7.92	AIR

FIG. 2 TEMPERATURE PROFILES OF GAS ANALYSIS FIRINGS

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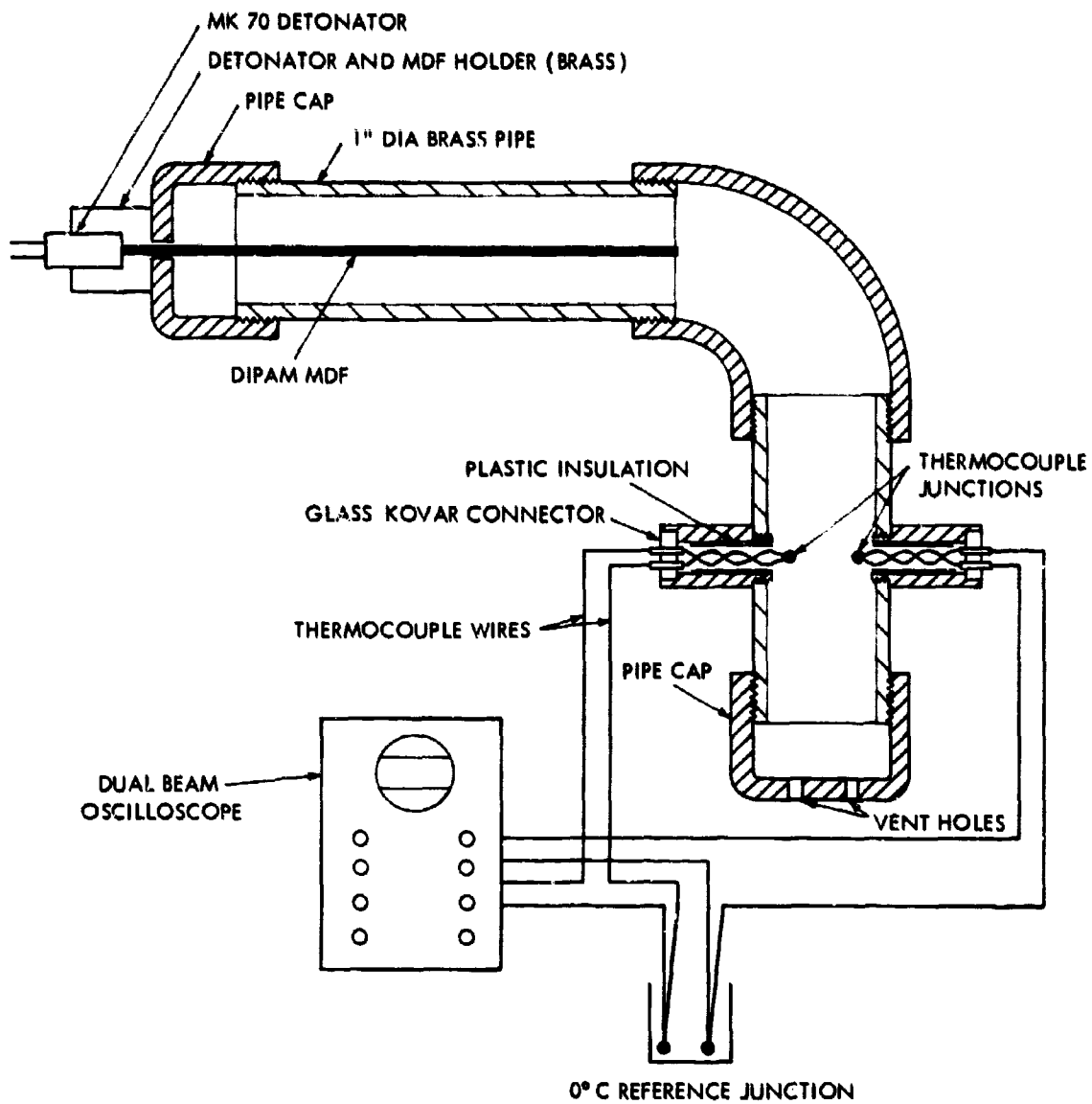


FIG. 3 TEMPERATURE STUDY APPARATUS

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TABLE III
TEMPERATURE STUDY RESULTS

Core Load	Wt. DIPAM	ΔT	Avg. ΔT
2.1 grain/ft	1.05 grain	6.0°	6.7°
2.1 grain/ft	1.05 grain	10°	
2.1 grain/ft	1.05 grain	4.0°	
10 grain/ft	5 grains	46.5°	41.7°
10 grain/ft	5 grains	46°	
10 grain/ft	5 grains	32.5°	
15 grain/ft	7.5 grains	76°	63°
15 grain/ft	7.5 grains	63°	
15 grain/ft	7.5 grains	64°	
15 grain/ft	7.5 grains	49°	

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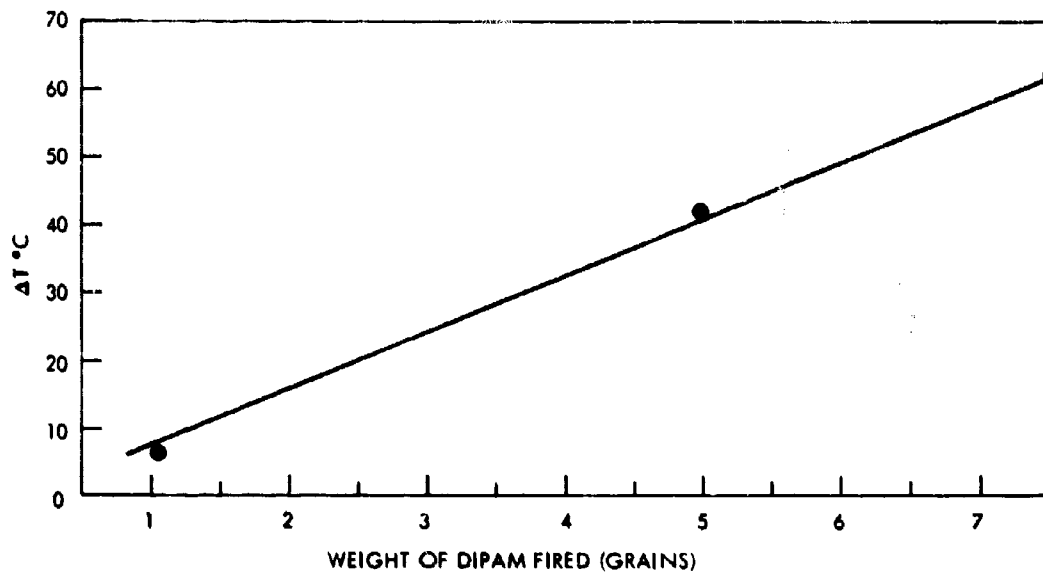


FIG. 4 TEMPERATURE STUDY RESULTS

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We surmise that the temperature trace observed in sample D was a complete anomaly not only on the basis of the reasoning above, but also because from Figure 2 it can be seen that the cooling time constant for D was much shorter, indicating a greater rate of cooling. Yet we can see no way that there could have been enough of a physical change in the experiment to cause such an alteration in the cooling rate.

CONCLUSIONS

Figure 5 shows the approximate relation of the CO_2/CO mole ratio versus the O_2/HE mole ratio for DIPAM and RDX. Other oxygen deficient explosives would be expected to show similar curves. As the oxygen available upon detonation decreases, the products contain greater amounts of carbon monoxide and free carbon. The appearance of sooty black solid products can be used as a qualitative indication (for DIPAM) that the CO_2/CO ratio in the gaseous products is fairly low. This, of course, is the undesirable tendency since the body can tolerate about 400 times as much CO_2 as CO for extended lengths of time.*

Although we do not have any data which tell us exactly what reactions do take place, we do have a basis for making pessimistic estimates of the toxicity due to CO_2 and CO. The following scheme is suggested:

- a. Determine the ambient temperature and pressures, and volume of the life support space into which product gases may be vented.
- b. Determine the number of moles of explosive which, by the design of the system, may produce the product gases.
- c. Estimate the O_2/HE mole ratio for the gases sufficiently close to the explosive to enter into afterburning reactions.
- d. Assume that all of the carbon in the molecule of explosive will yield either CO or CO_2 , or a combination of the two. The most pessimistic assumption is, of course, that it will all be converted to CO. However, the graph of Figure 5 will permit a more realistic estimate.
- e. From steps (b) and (d) above compute the number of moles of CO_2 and/or CO evolved.

*Submarine atmospheric environment limits are 10,000 ppm of CO_2 for 90 days and 25 ppm of CO for 90 days at 15 psia (NavShips 250-694-1, Rev. 1 of Sep 1962). It is the opinion of authorities at the National Naval Medical Center that these limits would represent a greater margin of safety at an ambient pressure of 7 psia.

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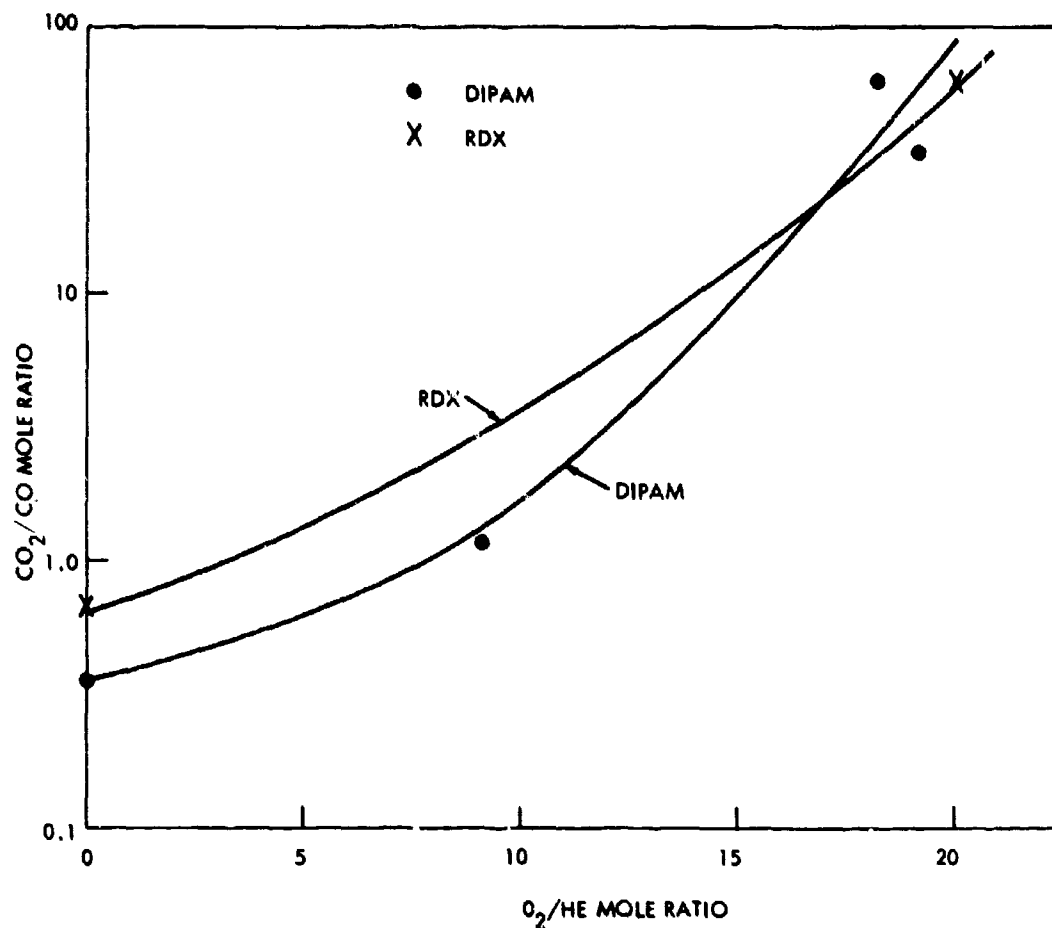


FIG. 5 EFFECT OF ATMOSPHERIC OXYGEN ON CO_2/CO BALANCE

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- f. From step (a) compute the number of moles of air already present.
- g. From steps (e) and (f) compute the contamination levels.

NOTE: Remember that the toxicity levels are quoted on a volume basis.

Oxygen deficient explosives confined in structures such as MDF react with oxygen in the atmosphere during and/or immediately after detonation. Products of detonation vary with the amount of oxygen available. Both DIPAM and RDX showed considerable formation of carbon monoxide when fired in an absence of atmospheric oxygen, as might be the case in space or high-altitude applications. Depending on the total amount of explosive, the products of explosion of MDF loaded with oxygen deficient explosive could be of sufficient carbon monoxide content to be harmful to human beings near by. It should be remembered that both CO_2 and CO are toxic and that, whatever the high explosive used, there will be a formation of both of these gases as well as other noxious or toxic materials.

RECOMMENDATIONS

A more thorough study of the detonation products of oxygen deficient explosives, including a quantitative determination of all gaseous and solid products, should be very informative. We would expect to be able to demonstrate that greater quantities of explosives would be permissible since we do not expect all the carbon atoms to be converted to CO_2 and/or CO . Detonation products for other explosives under other conditions and atmospheres should give valuable data useful in the better understanding of the detonation behavior of explosives. No studies have been made on the nitrogen oxides and metal products that also can present toxic hazards. For a thorough study, those should not be overlooked.

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		ROLE	WT	ROLE	WT	ROLE	WT
		Boosters, Mild Detonating Fuse Couplers, Mild Detonating Fuse Detonation Products of Explosives Fuses, Mild Detonating Explosives Explosives, oxygen deficient Airplane, F-111 crew module Toxicity, explosive products					

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14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical content. The assignment of links, roles, and weights is optional.

UNCLASSIFIED
Security Classification

<p>Naval Ordnance Laboratory, White Oak, Md. (NOL technical report 65-114) DETONATION PRODUCTS OF OXYGEN DEFICIENT EXPLOSIVES (U), by C. B. Root and J. N. Ayres. 25 Oct. 1965. 15p. illus., tables. NOL task 787/NASA.</p> <p>CONFIDENTIAL</p> <p>Mild detonating fuse containing oxygen deficient explosives showed considerable formation of carbon monoxide when fired in absence of atmospheric oxygen. Since this might be the case in space or high altitude applications, the detonation products of MOP loaded with oxygen deficient explosives could contain sufficient carbon monoxide to be harmful to mankind. A method is given for estimating the toxicity from carbon monoxide and carbon dioxide when oxygen deficient explosives are detonated in confined structures.</p>	<p>1. Fuses, Mild detonating Explosions - Toxicity</p> <p>I. Title</p> <p>II. Root, Charles B.</p> <p>III. Ayres, James N., Jr. author</p> <p>IV. Prefect</p> <p>Abstract card is unclassified.</p>
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